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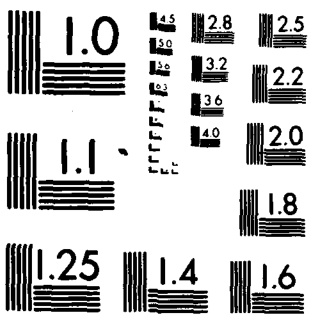

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THE DISSEMINATION AND COMBUSTION OF UNCONFINED LIQUEFIED NATURAL GAS CLOUDS

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FINAL REPORT

MAY 1979

Prepared for

U.S. DEPARTMENT OF TRANSPORTATION
United States Coast Guard
Office of Research and Development
Washington, D.C. 20590

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16. Abstract

A series of experimental tests were performed in the field to:

1. explosively disseminate liquefied natural gas (LNG) to form an unconfined cloud of measurable size and shape;

2. transfer a detonation wave from a different chemical cloud, but one known to support detonation, into an LNG cloud, and

3. observe and measure the effects of the transferred detonation wave in the unconfined LNG cloud.

Based on the results of these feasibility tests, additional experiments are recommended.

A two-cloud detonation transfer technique has been used to study the ability of an unconfined LNG cloud to support detonation. In this technique, two clouds are generated and the LNG cloud serves as the test cloud. The second cloud, the driver

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cloud, is composed of an easily detonable material and is used to generate the detonation wave. For these tests, propylene oxide was utilized as the driver cloud. A detonator in the driver cloud serves as the initiation source.

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High speed (~4000 frames/second) and the medium speed (~400 frames/second) cameras and pressure transducers served as diagnostics. The absolute radiometric output from the unconfined LNG cloud can be determined since calibration step wedges were used with films from selected cameras.

The detonation wave produced in the PO/air cloud was observed to decay as it progressed through the LNG/air cloud. The observed decay can occur for several reasons; namely,

- the temperature environment that exists within the LNG cloud
- the failure to maintain the critical energy, E_c, necessary to support combustion (detonation)
- the composition of the LNG/air cloud

Each of these factors is discussed in the report. It is not possible, with the limited number of tests, to select a single mechanism that uniquely explains the experimental observations.

Temperature influences a wide range of factors associated with detonation wave propagation in unconfined LNG/air clouds (e.g., critical energy, chemical kinetics, detonation limits, sensitizer behavior, etc.). Further studies should be performed to explore the ramifications of utilizing the lowered temperatures associated with LNG to minimize the environmental effects of LNG spills and combustion.

As a result of this program it is recommended that additional tests be performed to:

1. check the hypothesis that lowered temperatures in unconfined LNG or other chemical clouds contribute to the decay of propagating detonation waves and can be used to minimize environmental hazards
2. characterize spatially and temporally the dissemination and reaction phases of unconfined LNG clouds
3. compare the propagation of detonation waves in unconfined LNG clouds, both in the laboratory and the field
4. study the effect of both temperature and composition on the propagation of detonation waves in unconfined LNG clouds

5. utilize the two-cloud detonation transfer technique for studying the propagation of detonation waves in unconfined chemical clouds. Properly sized unconfined driver and test clouds can be used for the studies.

Abstract

A series of experimental tests were performed in the field to:

1. explosively disseminate liquefied natural gas (LNG) to form an unconfined cloud of measurable size and shape
2. transfer a detonation wave from a different chemical cloud, but one known to support detonation, into an LNG cloud
3. observe and measure the effects of the transferred detonation wave in the unconfined LNG cloud

Based on the results of these feasibility tests, additional experiments are recommended.

A two-cloud detonation transfer technique has been used to study the ability of an unconfined LNG cloud to support detonation. In this technique, two clouds are generated and the LNG cloud serves as the test cloud. The second cloud, the driver cloud, is composed of an easily detonable material and is used to generate the detonation wave. For these tests, propylene oxide (PO) was utilized as the driver cloud. A high explosive detonator in the driver cloud serves as the initiation source.

High speed (~4000 frames/second) and medium speed (~400 frames/second) cameras and also pressure transducers served as diagnostics. The absolute radiometric output from the unconfined LNG cloud can be determined since calibration step wedges were used on films on selected cameras.

The detonation wave produced in the PO/air cloud was observed to decay as it progressed through the LNG/air cloud. The observed decay can occur for several reasons; namely,

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- the composition of the LNG/air cloud

Each of these factors is discussed in the report. It is not possible, with the limited number of tests, to select a single mechanism that uniquely explains the experimental observations.

Conclusions:

The following conclusions were reached as a result of these tests:

(1) An explosively disseminated LNG cloud failed to support a detonation wave because of low temperatures within the cloud.

(2) Other factors can also be important with regard to the ability of an explosively disseminated LNG cloud to support detonation, but the role of these factors could not be determined in the present experiments. These factors include LNG spatial concentration gradients, phase distribution, drop or particle size distribution, and drop or particle velocity distribution within the cloud.

Recommendations:

Temperature influences a wide range of factors associated with detonation wave propagation in unconfined LNG/air clouds (e.g., critical energy, chemical kinetics, detonation limits, sensitizer behavior, etc.). Further studies should be performed to explore the ramifications of utilizing the lowered temperatures associated with LNG to minimize the environmental effects of LNG spills and combustion.

As a result of this program it is recommended that additional tests be performed to:

1. check the hypothesis that lowered temperatures in unconfined LNG or other chemical clouds contribute to the decay of propagating detonation waves and can be used to minimize environmental hazards

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4. study the effect of both temperature and composition on the propagation of detonation waves in unconfined LNG clouds

5. utilize the two-cloud detonation transfer technique for studying the propagation of detonation waves in unconfined chemical clouds. Properly sized unconfined driver and test clouds can be used for the studies.

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1.0 Introduction

The question of the detonability hazard from unconfined liquefied natural gas (LNG) clouds has environmental implications for the materials safe handling, storage, and transportation. Experiments on unconfined LNG spills have failed to substantiate whether LNG will support an unconfined detonation wave. A recent review by Schneider summarizes in detail the status with respect to field tests performed to test the burning and detonability of LNG clouds.[1] Calculations by Bull and Boni and Wilson conclude that large amounts of high explosive (22Kg and 10^4 to 10^6 Kg of tetryl, respectively) are necessary in order that fuel/air clouds composed of pure methane fuel support detonation at room temperature.[2,3]

The studies which have been performed to date were concerned with determining the detonability of LNG clouds which are the result of an accidental spill. The scenarios generally assume at least partial evaporation of the spill, so that the LNG cloud is above its' boiling temperature of 109°K. In fact many studies have been predicated on the assumption that the LNG cloud is at ambient temperature.

One event which has not yet been considered is that wherein the LNG cloud is formed by explosive dissemination. Such an event could be the result of terrorism or sabotage, acts of war, an airplane crash, or natural catastrophes such as lightening strikes or earthquakes. Perhaps the most credible accident which would result in explosive dissemination of LNG is a consequence of the accidental leak or spill which is receiving so much attention at the present time. In the event that accidental ground or water spills prove to present an explosion hazard, then the possiblity of a spill detonating and disseminating LNG from neighboring storage

tanks becomes very real. Avoidance of these sympathetic detonation chain reactions is a major concern in the explosives industry and also at military installations, where storage areas are widely separated. Thus the detonability of explosively disseminated LNG clouds is a safety problem which should be addressed.

Another important consideration is whether cold LNG clouds are less of an explosion hazard than those which are at ambient temperature. This information is a measure of the time available to neutralize spills or evacuate personnel from the area. This is particularly true for the case of explosive dissemination, where the LNG will evaporate much more slowly than in the case of a ground or water spill.

As a result of experience gained from studying the combustion of unconfined fuel/air clouds, Geo-Centers, Inc., performed a feasibility study on the ability of an unconfined LNG cloud to support a detonation wave. As part of the program, field tests were performed to:

1. characterize the explosive dissemination of LNG to form an unconfined cloud
2. transfer a detonation wave from a cloud known to support detonation into an LNG cloud
3. observe the effects of the transferred detonation wave in the unconfined LNG cloud

The tests were performed at the Cable Test Facility, Coyote Test Station, Sandia Laboratories, Albuquerque, New Mexico.

This report reviews the protocol and results of preliminary tests and the unconfined LNG dissemination and detonation tests, discusses the results of the LNG tests, and recommends further tasks to determine the safety and hazard associated with accidents and spills that produce combustible, unconfined LNG clouds.

2.0 Preliminary Tests

Prior to actually testing the dissemination and detonability of LNG, a series of proof (or feasibility) tests were conducted. The objectives of these preliminary tests were to:

1. select a safe container (Dewer) for the LNG
2. determine the explosive dissemination characteristics of non-reactive cryogenic liquids.
3. test the explosive burster to insure that it operates at liquid nitrogen temperatures
4. select the appropriate diagnostics available and test these systems as part of the proof tests.

Liquid nitrogen (LN) was chosen as the non-reactive cryogen. LN has the advantage of having a boiling temperature lower but close to that of LNG ($77^{o}K$ versus $109^{o}K$ respectively).

Safety and handling considerations mandated that initially a Dewar be used to contain the cryogens during the tests. Two different Dewars were tested and Table 2.1 compares their characteristics. Three proof tests to measure cryogen containment and dissemination were performed. Table 2.2 summarizes the test conditions while Table 2.3 summarizes the camera conditions and settings used for the three tests.

The scored, stainless steel Dewar (Cryenco) (see Table 2.2),containing LN, only bulged when the burster was initiated, but did not disintegrate. LN escaped, but did not form a cloud

Table 2.1

Comparison of Dewars Chosen for Proof Testing

	Dewar 1	Dewar 2
Manufacturer	Cryenco	Union Carbide
Model	350	UC-17
Capacity (Liters)	25	17
Construction (outer shell)	Stainless Steel	Aluminum
(inner shell)	Stainless Steel	Fiberglass
LNG Capacity (lbs)	22.8	15.5
Height (inches)	23	21
Outside Diameter (inches)	15	14
Test Configuration	Scored	Scored and Unscored

Table 2.2

Summary of Proof Test Conditions

	Test 1	Test 2	Test 3
Date of Test	8/15/78	9/1/78	9/18/78
Dewar	Cryenco	Union Carbide	Union Carbide
Scored or Unscored	Scored	Scored	Unscored
Second Cloud	None	Water	Propylene Oxide
Fuel/Burster Ratio	200	200	200

Table 2.3

Camera Settings and Characteristics for Proof Tests*

Station	View	Speed (fps)	Test 1	Test 2	Test 3
1	OH	4000	f/2.8, 1" lens	f/2.8, 1" lens	f/2.8, 1" lens
2	OH	4000	f/2.8, 2" lens	f/2.8, 2" lens	f/2.8, 12 mm
3	S	4000	f/2.8, 6" lens	f/2.8, 6" lens	f/2.8, 6" lens
4	S	4000	f/2.8, 35 mm	f/2.8, 35 mm	f/2.8, 35 mm
5	S	4000	f/2.8, 1" lens	f/2.8, 1" lens	f/2.8, 1" lens
6	OH	400		f/5.6, 1" lens	f/5.6, 1" lens
7	S	400		f/5.6, 1" lens	f/5.6, 1" lens

* film used was Ektachrome EF color film; all cameras used are 16 mm; 400 fps cameras are Millikan, while 4000 fps cameras are Hycam or Fastax

OH = Overhead

S = Side

fps= frames per second.

suitably shaped for testing. The scored, aluminum Dewar (Union Carbide) broke apart symmetrically upon burster initiation. A 28 to 29 foot diameter cloud was formed at 110 to 125 milliseconds following dissemination. The unscored, aluminum Dewar bulged, in a manner similar to the scored stainless steel Dewar, but did not disintegrate. The LN formed a non-uniform cloud with a significant quantity of LN escaping in the upward direction (through the top of the Dewar). As a result of these tests, a scored, aluminum/fiberglass 17 liter Dewar (Union Carbide) was chosen as the preliminary container for the LNG tests.

Bursters are normally use rated starting with dry ice temperatures. Since the proposed tests involve cryogenic fluids at temperatures less than the rated temperatures, a series of burster sensitivity and liquid nitrogen cold soak tests were performed. No difficulties were encourntered during the tests, and it was concluded that the burster would function normally at cryogenic temperatures.

3.0 Unconfined LNG Tests

A series of seven (7) field tests were performed at Sandia Laboratories, Albuquerque, New Mexico, which consisted of:

1. explosively disseminating LNG to form an unconfined cloud
2. forming and transferring a detonation wave into the unconfined LNG cloud.

The test schedule was set around the availability and delivery of LNG to the test facility in Albuquerque. A 100 gallon LNG container, illustrated in Figure 3.1, was obtained and used as the major LNG container and source for filling the Dewars. The container was obtained from Gibson Cryogenics, Lakeside, California; and was safety certified for containing LNG. A 50 psig safety valve was an integral part of the container. During the week of the tests, the pressure within the container did not rise above 35 psig.

This study utilizes a two-cloud detonation transfer technique for testing the ability of the unconfined LNG cloud to support a detonation wave. In this technique, two clouds are generated. One cloud serves as the test cloud, which for this series of tests, contains the LNG. The second cloud, the driver cloud, is composed of an easily detonable material, and is used to generate the detonation wave. For these tests, the second cloud utilized propylene oxide (PO) as the detonable material. To insure transfer of the wave, the two clouds are overlapped. This cloud configuration is the unconfined analogue of the shock

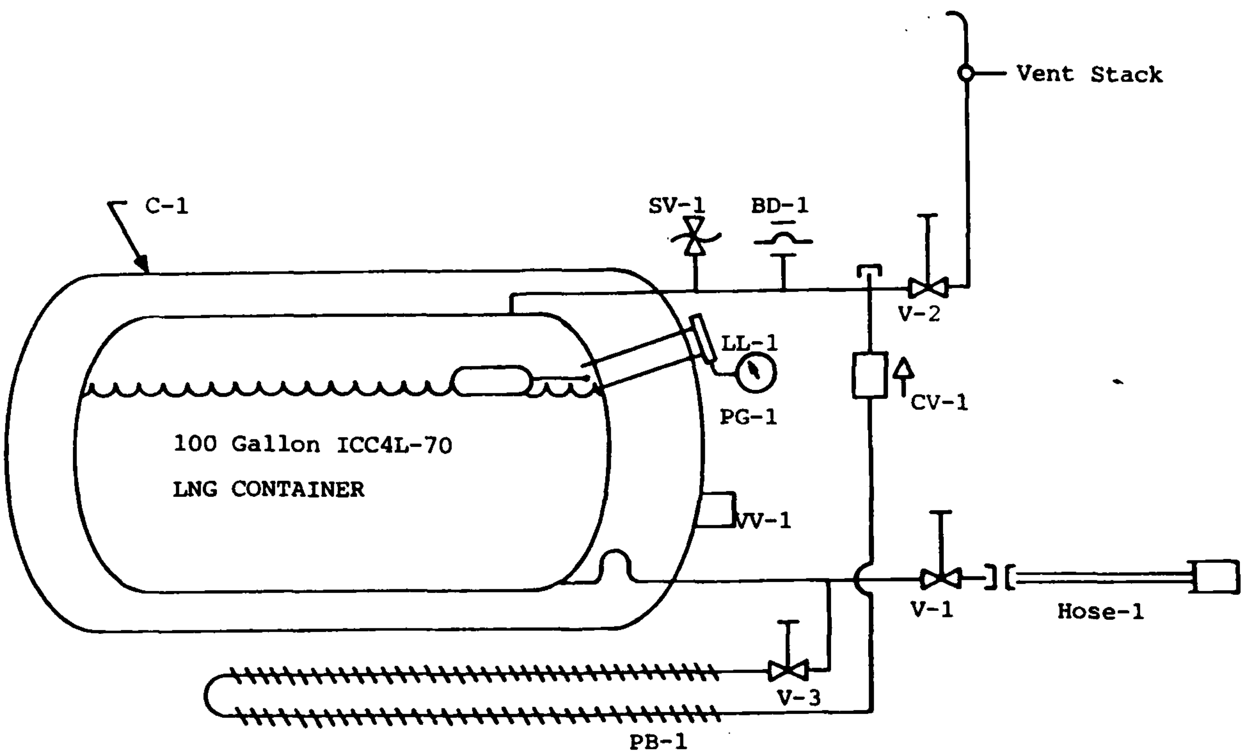


Figure 3.1   Schematic Diagram - 100 Gallon LNG Container

Legend	
V-1	Fill and drain valve
V-2	Manual vent valve
V-3	Pressure build valve (manual)
SV-1	Safety Valve Set - 50 psig
BD-1	Burst disk 77 psig
LL-1	Liquid level gauge
PG-1	Pressure Gauge 0-100 psig
CV-1	Check Valve
VV-1	Vacuum Valve - Relief and evacuate
C-1	Container tank - 100 gallon
Hose-1	Flexible metal hose, 1/2"
PB-1	Pressure build coil

tube commonly found in the laboratory. In these field tests, the PO cloud serves as the driver while the LNG cloud serves as the driven section. The detonator in the driver cloud is the initiation source.

Figure 3.2 gives the general layout for the tests. The LNG Dewar was located at ground zero. The PO container and the detonator were located to the west (W) of ground zero. Pressure transducers, seven (7) in number, were located at P 17W, P 6W, P 5E, P 10E, P 15E, P 20E, and P 25E relative to ground zero (see Figure 3.2). They were flush mounted in concrete blocks placed in the ground. The LNG Dewar, PO container, and detonators were placed on stands which had vertical black and yellow markers on them for dimension identification. The markers were 4 feet high and were painted in alternating 1 foot square yellow and black colors. Circles were marked at radii of 5, 10, 15, 20, and 25 feet from ground zero. In addition, two (2), twelve (12) foot overhead markers were extended east from ground zero. These boards contained 2 feet long by 1 foot wide alternating yellow and black rectangles. The bursters were placed in each of the containers just prior to the actual test.

Table 3.1 lists the test conditions for the seven (7) tests including the distance of the PO container and detonator from the LNG (ground zero), the height of the containers above the ground, the type of container for the LNG, the fuel/burster ratio for dissemination of the LNG, and the detonator firing time following LNG dissemination. For test number 6, the PO was disseminated 890 milliseconds after LNG dissemination and the detonator was fired 1000 milliseconds (1 sec) after dissemination of the LNG.

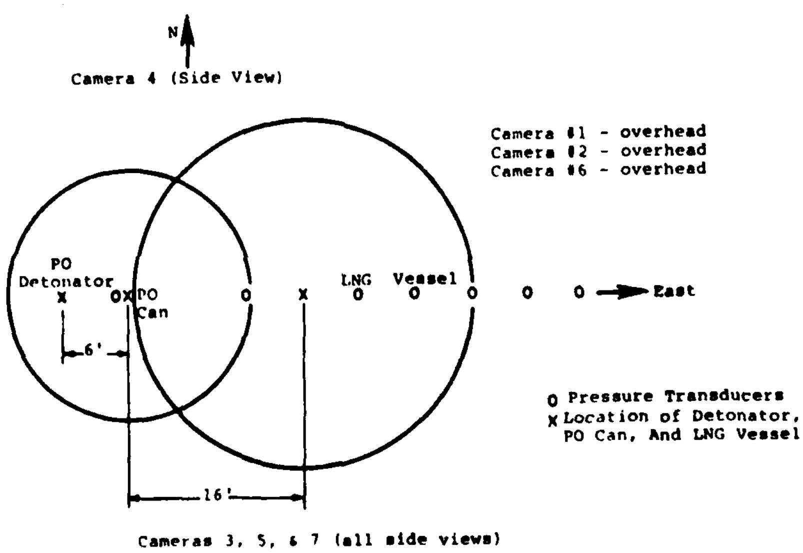


Figure 3.2 - General Test Layout (Test 1)

Table 3.1

Test Conditions for the Unconfined LNG Dissemination and Detonation Tests

Test No.	Location* PO Container(ft)	Location* Detonator(ft)	Height Above Ground(ft)	Container Type	Detonator time(msec)	Fuel Burster Ratio
1	16	20	4	Scored Dewar	110	100
2	20	26	4	Scored Dewar	110	100
3	20	26	4	5 gallon plastic	110	100
4	20	26	4	Scored Dewar	110	200
5	20	26	4	Scored Dewar	110	50
6	20	26	4	Dewar(Inner Fiber-glass container)	1000 (PO=890)	50
7	25	31	3	Scored Dewar	160	50

* Relative to LNG container

Pressure transducers and photographic cameras served as the main diagnostic instruments. Table 3.2 summarizes the camera characteristics for the seven tests.

For quantitative radiometry, calibration step wedges were exposed on selective Ektachrome EK type 7421 film records. A side view and/or overhead view camera in each test, beginning with test number 2, was selected to use the calibrated film (see Table 3.3). The wedges were affixed to the head and tail of the appropriate films from each test and processed with the film. Thus,absolute radiometric output from the unconfined LNG cloud can be obtained using the films from these cameras , although this was not done.

During the first test, the electrical line to the detonator was severed during the dissemination phase. The detonator line was encased in a metal pipe and buried for the remainder of the field tests. In addition, the overlap between the two clouds was greater than anticipated, and the distance between the LNG Dewar and the PO container was increased (see Table 3.1).

Generally, a scored aluminum/fiberglass Dewar was used to contain the LNG. However, to test the size of the cloud as a function of container, two variations were made. In test number 6 the aluminum outer shell was removed, and only the fiberglass inner container was used. In the other variation, (test number 3), a five gallon, high impact styrene bottle was used to contain the LNG. Each container produced a slightly larger cloud than the two layer Dewar (the results are reported in Section 4.0).

TABLE 3.2

CAMERA SETTINGS AND CHARACTERISTICS FOR LNG TESTS*

STATION	VIEW	SPEED (FPS)	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5	TEST 6	TEST 7
1	OH	4000	F/2.8, 1" LENS	F/2.8, 1" LENS	F/2.8, 1" LENS	F/2.8, 1" LENS	F/2.8, 1" LENS	F/3.5, 1" LENS	F/2.8, 13 MM
2	OH	4000	F/2.8, 2" LENS	F/2.8, 40 MM	F/2.8, 40 MM	F/2.8, 40 MM	F/2.8, 40 MM	F/3.5, 40 MM	F/2.8, 1" LENS
3	S	4000	F/2.8, 6" LENS	F/2.8, 6" LENS	F/2.8, 6" LENS	F/2.8, 6" LENS	F/2.8, 6" LENS	F/3.5, 6" LENS	F/2.8, 6" LENS
4	S	4000	F/2.8, 1" LENS	F/2.8, 1" LENS	F/3.5, 1" LENS	F/2.8, 1" LENS	F/3.5, 1" LENS	F/3.5, 1" LENS	F/3.5, 1" LENS
5	S	4000	F/2.8, 1" LENS	F/2.8, 13 MM	F/2.8, 13 MM	F/2.8, 13 MM	F/2.8, 13 MM	F/3.5, 13 MM	F/2.8, 13 MM
6	OH	400	F/5.6, 1" LENS	F/5.6, 1" LENS	F/4.0 1" LENS	F/4.0 1" LENS	F/4.0 1" LENS	F/5.6, 1" LENS	F/5.6, 15 MM
7	S	400	F/5.6, 13 MM	F/5.6, 13 MM	F/5.6, 13 MM	F/5.6, 13 MM	F/5.6, 13 MM	F/5.6, 13 MM	F/5.6, 13 MM

* FILM USED WAS EKTACHROME EF COLOR FILM EXCEPT AS NOTED IN TABLE 3.3; ALL CAMERAS ARE 16 MM; 400 FPS CAMERAS ARE MILLIKAN, WHILE 4000 FPS CAMERAS ARE HYCAM OR FASTAX.

FPS = FRAMES PER SECOND

OH = OVERHEAD

S = SIDE

Table 3.3

Summary of Cameras Selected to Use Calibrated Film

Test No.	Station No.	View	Speed (fps)	Comments
1				No calibrated film
2	1	OH	4000	Film jammed
	4	Side	4000	Good data
3	4	Side	4000	Good data
4	4	Side	4000	Good data
	6	OH	400	Good data
5	4	Side	4000	Good data
	6	OH	400	Good data
6	6	OH	400	Good data
7	4	Side	4000	Good data
	6	OH	400	Good data

Two gas chromatographic analyses were carried out to determine and monitor the LNG purity. Before the first test, the LNG was sampled from the vent valve and represented a sampling of the vapor above the LNG. The second sample was taken between the sixth and seventh tests and was sampled through the LNG extraction hose. This sample represented liquid LNG which vaporized. The results of these two analyses are contained in Appendix A. Ideally, we would have wished a liquid sample, but this was not practical at the time. The second sample extracted more closely represents the composition of the LNG we received for our tests.

4.0 Discussion of Results From LNG Tests

Unconfined LNG and PO clouds were generated in seven (7) tests. Figures B1 to B7, in Appendix B, give the temporal dissemination behavior of the LNG clouds. The films from the overhead cameras were used to obtain the radial extent of the clouds. The side view films produce information on vertical cloud extent and shape. Figure 4.1 compares the average LNG cloud size obtained from the tests at 110 milliseconds following LNG dissemination. The plastic container and single wall Dewar both produce slightly larger clouds than obtained from the double wall, scored Dewar at an equivalent fuel/burster ratio. The LNG clouds continued to expand with time but at a slower rate (close to the diffusion limiting case) for times exceeding 80 to 100 milliseconds. This expansion causes a changing global fuel/air ratio within the cloud. LNG dissemination in Test 6 (the single wall Dewar) produced a cloud with an average diameter of 28 feet at 110 milliseconds and an average diameter of 34 feet at 1000 milliseconds (1 sec).

We have observed from our earlier fuel/air work with unconfined clouds that cube root scaling of the diameter and height of the cloud is followed.[4] The unconfined LNG clouds produced in this study generally conform to this scaling law.

The films from the overhead cameras were used to track the progress of the detonation wave moving from the PO cloud through the overlap region into the LNG cloud. The side view cameras produce a distorted picture of the progress of the wave because of the lack of proper radial perspective. Table

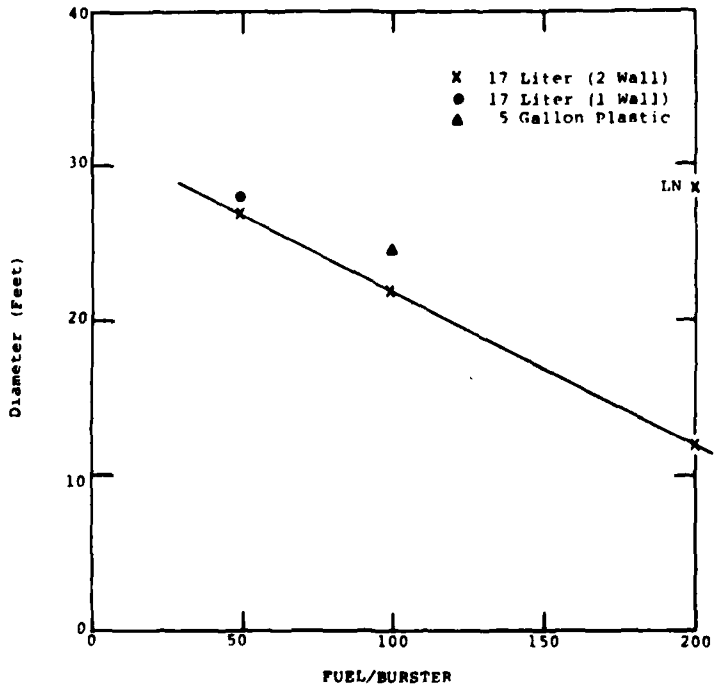


Figure 4.1 LNG Cloud Diameters at 110 msec after burst.

4.1 summarizes the changes measured in the dimensionless velocity (Mach number) of the wave as it progresses from the PO cloud, through the overlap region, and through the LNG cloud. As Table 4.1 indicates, close to a Mach 6 wave is produced in the PO/air cloud. This wave decays to approximately Mach 4 in the overlap region. The wave further decays to approximately Mach 1.5 as it progresses through the LNG cloud.

Table 4.2 summarizes the maximum pressure observed at the seven (7) transducer stations for each of the tests. The five (5) gauges on the east side of the Dewar did not measure pressures in excess of 40 psi. These values are consistent with the measurements of the decaying wave velocity tabulated in Table 4.1. The two (2) transducers on the west side of the Dewar did measure, in some instances, significantly higher pressures. In several of the tests (e.g., tests 2, 3 and 5), pressures in excess of 200 psi were recorded. In particular, the high pressures recorded at station P 17W in tests 3 and 5 also happen to coincide with the high wave velocities in the PO cloud that we measured from the films. The decay of the detonation wave was observed in both the films and the pressure transducer recordings.

The observed decay of the detonation wave as it passed from the PO/air cloud into and through the LNG/air cloud can occur for a number of reasons,

- the temperature environment that exists within the LNG cloud
- the failure to maintain the critical energy, E_c, necessary to support detonation
- the composition of the LNG/air cloud

Table 4.1

Measured Wave Propagation*

Wave Mach Number

Test No.	PO	Overlap		LNG
1		Detonator Failed		
2		4.5		1.3
3	5.4	3.0		1.5
4		4.8		2.1
5	6.5	4.0	2.9	1.6
6	Detonation Did Not Develop			
7		3.9	1.8	1.3

* Inferred From Overhead Cameras (4000 frames/second)

Table 4.2

SUMMARY OF MAXIMUM PRESSURE RECORDED FROM TRANSDUCERS*

Test No.	Distance From Dewar To PO (ft)	Distance From Dewar To Detonator (ft)	Pressure Transducer Station (LNG Dewar Ground Zero)						
			P 17 W**	P6W	P5E	P10E	P15E	P20E	P25E
1	16W	20W	D E T O N A T O R		F A I L E D				
2	20W	26W	++ (~175)+	205 (~220)	27	14	10	7	-
3	20W	26W	230	128	40	18	12	14	13
4	20W	26W	135	160	32	18	13	9	8
5	20W	26W	280 (275)	68 (80)	35	20	14	12	8
6#	20W	26W	16	-	-	-	-	-	-
7	25W	31W	120 (175)	40	14	12	10	9	6

* Pressure in psi

** P 17W = Pressure transducer 17 feet west of LNG Dewar; E = east.

++ Problem with print out; data not reliable.

\+ ( ), Inferred from Visicorder results on day of test.

\# Detonation did not develop.

It is not possible, with the limited tests we performed, to select a single mechanism that uniquely explains the experimental observations.

Measurements of the temperature within the LNG cloud were not performed as part of this study. In the approximately 110 to 160 milliseconds between dissemination and detonation of the LNG cloud, the cloud has not had sufficient time to totally evaporate. The LNG cloud is opaque and appears to be optically thick with considerable quantities of liquid LNG present. In contrast to the LNG case, the PO cloud is initially opaque, but becomes transparent soon after dissemination ($t < 50$ milliseconds). Temperature measurements in PO clouds indicate that initially the temperature within the cloud decreases approximately 50°F (71°F to 20°F), eventually returning to the ambient value.[5] The dispersed LNG in our tests has not had sufficient time (up to 1 second) to equilibrate to the ambient temperature. Thus, if the temperature within the LNG cloud is less than ambient, the detonation wave transferring into the "colder" LNG should be affected by this changed environment, particularly if the internal temperature of the LNG cloud is 110 to 150°K.

Since chemical reaction and kinetic considerations are temperature dependent, one expects changes in wave propagation behavior as the ambient or medium temperature changes. If all of the liquid LNG within the cloud has not evaporated, then one expects temperatures of approximately -160°C (113°K) to exist within the LNG cloud. The overlap regime may have

a slightly higher temperature due to the mixing of ambient PO and air and the colder LNG. Temperature may be one of the causes of the decay of the detonation wave in the overlap region, although compositional effects (fuel/air ratio, methane chemistry) cannot be ruled out.

The photographic records exhibit evidence that some condensation takes place within the overlap region. The condensate could be PO which has a freezing point of -104°C (169°K). The ambient temperature during these field tests was approximately 48°F (9°C).

Recent calculations on methane/air detonations lend support to the hypothesis concerning the effect of ambient temperature on the support of unconfined detonation.[6] As the ambient temperature of the methane/air cloud decreases, the mass of tetryl necessary to directly initiate a detonation wave in an unconfined environment increases. This is illustrated in Figure 4.2 where an order of magnitude (X10) increase in tetryl is necessary for each 100°K decrease in ambient temperature.

A two cloud detonation transfer technique has been employed in this study. This technique has several advantages over direct initiation. These are

1. large quantities of high explosive (HE) are not necessary since the detonation wave is produced in a cloud composed of an easily detonable material.
2. the size of the easily detonable (driver) cloud can be scaled according to the size of the test cloud. This has the advantage of being able to use a tailored, easily detonable driver cloud to test the detonability of the test cloud.

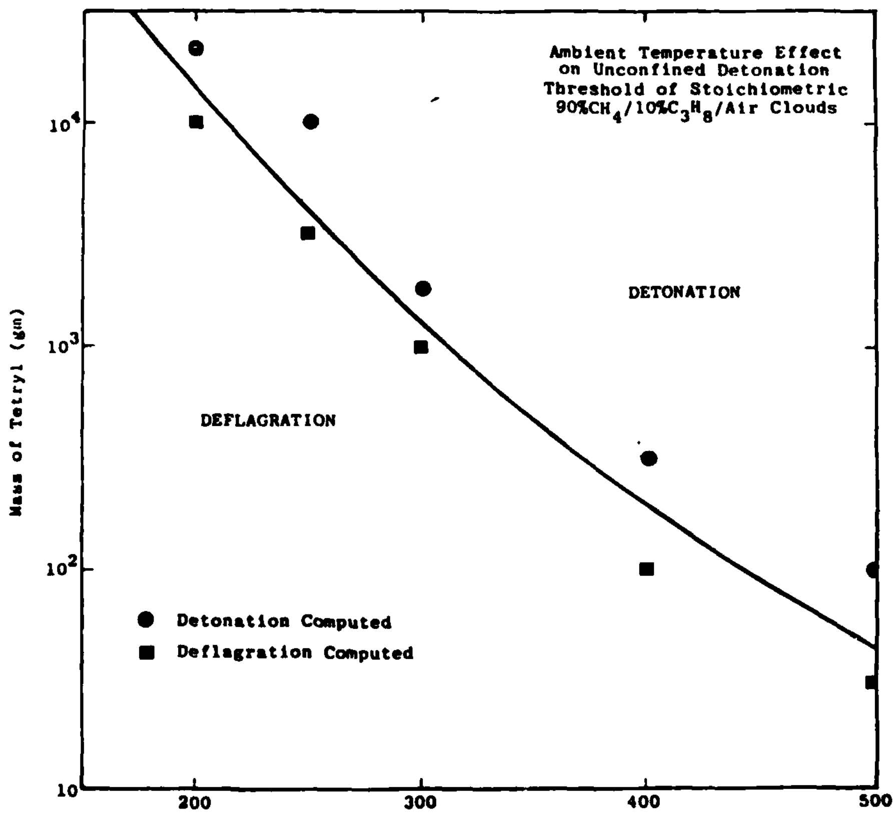


Figure 4.2 Effect of Ambient Temperature on Detonability (Reference 6)

For direct initiation of a detonation in an unconfined cloud, a critical energy (E_c) is needed to provide a blast wave having a critical Mach number (M_c) when the wave is at a critical radius (R_c). From blast wave theory, the relationship between E_c, R_c and M_c is [7]

$$R_c^3 = \frac{E_c}{M_c^2 \, J_o \, \kappa_\alpha \, p_o} \tag{1}$$

where p_o = ambient pressure
J_o = .593 and
$\kappa_\alpha = 4\pi$ for spherical waves

Thus, if E_c can be estimated, then R_c can be calculated. This is the critical radius that must be maintained if a detonation wave is to propagate in an unconfined cloud. In utilizing the two cloud technique to study detonability, we assume that if we know or can estimate the critical energy (E_c), a critical radius necessary to support detonation in both clouds can be estimated. The driver cloud is then sized to produce a tailored detonation wave that is transferred into the test or LNG cloud. If we use this model for the propylene oxide (PO) and LNG clouds produced in this study, then the PO energy was below the minimum necessary to sustain detonation in the LNG cloud.

Bull and Boni and Wilson have estimated the amount of tetryl necessary to detonate an unconfined LNG cloud.[2,3] The amount of tetryl estimated varies between 22 Kg and 10^4 to 10^6 Kg respectively. Table 4.3 compares the PO cloud size (radius) necessary to produce a Mach 5 detonation wave for equivalent amounts of tetryl between 10 Kg and 10^6 Kg. Also

Table 4.3

Comparison of Critical Radii for Quantities of Tetryl⁺

Tetryl Mass (Kg)	Equivalent Tetryl Critical Energy (Joules)	Critical Radius (m)	Quantity of PO (pounds)
10	4×10^{7}	1.6	1.0
22(**)	8.8×10^{7}	2.1	2.4
10^{2}	4×10^{8}	3.5	11.0
10^{3}	4×10^{9}	7.6	115.0
10^{4}(*)	4×10^{10}	16.3	1159.0
10^{5}(*)	4×10^{11}	35.1	
10^{6}(*)	4×10^{12}	75.7	

+ Calculations assume ambient temperature

** Bull's estimated value for critical initiating mass of tetryl

* Boni and Wilson's estimated values for critical initiating mass of tetryl

included are equivalent quantities of PO that are necessary to produce these unconfined clouds. The results given in Table 4.3 indicate that over the five (5) orders of magnitude change in tetryl mass, the equivalent critical radius of PO, calculated to sustain detonation, increases approximately a factor of 50. This is a consequence of the cube root scaling law.

Temperature, both ambient and behind a shock wave, influences the critical energy, E_c. Thus, a minimum critical energy must be maintained if the detonation wave is to be sustained.

According to Zel'dovich et. al., the critical energy, E_c, for direct initiation of spherical detonations is proportional to the induction time, τ, via [8]

$$E_c \sim \tau^3 \qquad (2)$$

The induction time is related to the Arrhenius expression via

$$\tau \; \alpha \; \exp \left[E_a/(RT) \right] \qquad (3)$$

where E_a = activation energy

R = gas constant (2 cal/mole)

T = temperature

For methane, E_a has a value of 48,000 cal/mole. Combining equations (2) and (3) leads to

$$E_c \; \alpha \left[\exp \left(\frac{24000}{T} \right) \right]^3 \qquad (4)$$

For Mach 4 and Mach 5 shock waves, the temperature behind the shock wave, $T = T_b$, varies with the ambient temperature, T_a, in ratios between 4.0 and 5.8 respectively. Table 4.4

Table 4.4

Comparison of Changes in the Induction Times and Critical Energies as a Function of Mach Number and Ambient Temperature

Number	$\frac{T_b}{T_a}$*	T_a (°K)	T_b (°K)	$\frac{\tau_b(T_a)}{\tau_b(T_a=300)}$	$\frac{(E_c)_{Ta}}{(E_c)_{Ta=300}}$
4	4.0	300	1200	1.00	1.00
		250	1000	5.46×10	1.63×10^{5}
		200	800	2.20×10^{4}	1.07×10^{13}
		150	600	4.85×10^{8}	1.14×10^{26}
5	5.8	300	1740	1.00	1.00
		250	1450	1.58×10	3.93×10^{3}
		200	1160	9.89×10^{2}	9.67×10^{8}
		150	870	9.78×10^{5}	9.35×10^{17}

T_b = temperature behind the shock wave

T_a = ambient temperature

compares the change in the critical energy calculated to support the indicated shock wave as the ambient temperature varies from 300 to 150°K. Also given in Table 4.4 is a comparison of the change in induction time as the ambient temperature changes. As noted from Table 4.4 and equation 2, the cube dependence of the induction time has a strong effect on the change in the critical energy as the ambient temperature and/or the temperature behind the shock wave changes. The critical energy necessary to support a Mach 4 detonation wave in methane changes by a factor in excess of 10^{20} as the ambient temperature changes from 10°C (283°K) to -160°C (113°K) (a factor of 2.5) while the critical energy changes by a factor in excess of 10^{15} for a Mach 5 detonation wave over the same ambient temperature range.

Composition of the LNG cloud can also affect the behavior of the detonation wave. Two major factors are important; namely

- the fuel/air ratio
- the presence of sensitizers which influence detonation wave behavior

A proper fuel/air ratio, within limits, must be maintained if the detonation wave is to propagate within the cloud. Although the detonation limits for methane/air mixtures are not known, the flammability limits are 5 to 15 volume percent (3 to 9 weight percent). The detonation limits, at the comparable temperature, should be narrower. We calculate that our global fuel/air ratio is probably on the lean side of stoichiometric; namely 3 to 5 weight percent based on measured cloud dimensions at 110 milliseconds following LNG dissemination.

Temperature should also affect detonation limits, with the limits becoming narrower as the ambient temperature decreases. White established that the flammability limits of a number of chemical vapors were widened as the initial temperature was increased.[9,10] While a number of investigators have recently been studying the detonability of unconfined methane/air mixtures at ambient temperatures, little work has been pursued concerning detonability of "colder" LNG/air mixtures. Since LNG spills would initially involve "cold" methane/air mixtures, the effect of detonability limits as a function of temperature should not be overlooked in examining LNG hazard and safety.

Bull et.al.,Boni and Wilson, and Matsui and Lee have all calculated critical energies necessary to support detonation in methane/air mixtures.[2,3,11] Bull et. al. estimate that 8.8×10^7 joules are necessary to support detonation waves in stoichiometric methane/air mixtures at ambient temperatures while Matsui and Lee calculate a critical energy of 2.3×10^8 joules for 12.3 methane percent by volume.[2,11] Boni and Wilson calculate that 4×10^{10} to 4×10^{12} joules are necessary to support detonation in stoichiometric methane/air mixtures at ambient temperatures. As the fuel/air ratio becomes leaner or richer than stoichiometric, a greater critical energy is necessary to support detonation. For fuel/oxygen mixtures, the detonability limits and the critical energy behavior as a function of fuel volume percent is summarized in Reference 11.

Sensitizers can influence the behavior of detonation waves.[4] Bull et. al. have recently studied the effect of ethane on the amount of tetryl necessary to support detonation

in methane/air mixtures with overall stoichiometric ratios of unity.[12] They find that increasing quantities of ethane (30 to 100% ethane in methane/ethane mixtures) decreases the amount of tetryl necessary to initiate detonation by a factor of 20. Similar behavior has been observed for additions of propane and butane to methane/air mixtures. While we found approximately 2.8% ethane, 0.5% propane, and 0.2% butanes (3.5% higher hydrocarbons) in our LNG, we would not expect this amount to make a major contribution to the decay of our detonation wave. However, the effects of large quantities of a sensitizer, such as ethane and propane on detonation wave behavior should be examined. These studies should be carried out at both ambient (25°C) and reduced (-160°C) temperatures. This would test the influence of temperature on the ability of sensitizers, present in some LNG's, to affect the propagation of detonation waves in LNG/air mixtures.

Temperature appears to be a strong influence in determining the hazard and safety associated with LNG. Examining the various factors associated with detonation wave propagation in unconfined LNG/air clouds (e.g., critical energy, chemical kinetics, detonation limits, sensitizer behavior, etc.) indicates that temperature could be used to effectively deal with LNG hazards.

5.0 Conclusions and Recommendations

The initial objectives of this study have been achieved; namely,

1. LNG has been explosively disseminated to form an unconfined cloud of measurable shape and size.
2. a detonation wave has been transferred from a cloud known to support detonation (PO) into an unconfined LNG cloud.
3. the effects of the transferred detonation wave have been observed and measured in the unconfined LNG cloud.

The detonation wave produced in the PO/air cloud was observed to decay as it progressed through the overlap region into the LNG/air cloud. The observed decay may be due to,

- the temperature environment that exists within the LNG/air cloud.
- a failure to maintain the critical energy, E_c, necessary to support detonation.
- the composition of the LNG/air cloud

Temperature within the LNG/air cloud is extremely important since it influences the chemical kinetics that occur, influences the critical energy necessary to support detonation and affects the detonation limits. If our conclusion about the importance of temperature is valid, it should be possible to take practical advantage of this phenomenon. Further studies should explore the ramifications of utilizing lowered temperatures to minimize the environmental effects of chemical spills. An instrumented test of a large quantity of LNG spilled in a contained dike and ignited would check the hypothesis.

Large, unconfined LNG clouds are not well characterized with respect to parameters such as localized temperature, composition, phase distribution, drop or particle size distribution, and drop or particle velocity. We recommend that tests on unconfined LNG clouds be performed to measure these parameters. Both spatial and temporal behavior should be measured. Both the dissemination and reaction phases involving the unconfined LNG cloud should be studied.

The results of this study and recent calculations indicate that additional effort is required to quantify the effects of temperature on unconfined detonation. LNG is one of the coldest substances presently stored, transported, and handled in bulk. Since it appears that the low temperature of the LNG (110°K) affects the propagation of detonation waves, this factor should be considered in any safety and spill or accident control program.

To test the effect of temperature on blast wave propagation in unconfined LNG clouds, laboratory and field tests should be performed. The propagation of shock waves through LNG (methane) at various temperatures in a laboratory shock tube can be used to guide the nature and direction of the unconfined field tests. Field tests using LNG clouds, with different internal cloud temperatures, could be performed to study detonation wave propagation. The final field test could be a large, unconfined, but contained LNG spill, which is ignited. Variation in ignition time following spill deployment should be studied and the results compared.

Calculations by Bull[2] Boni and Wilson[3], indicate that higher hydrocarbons (ethane, propane, butane, etc.) strongly influence

the detonability of LNG. We recommend that the effect of both cloud temperature and hydrocarbon composition of unconfined LNG clouds be simultaneously studied. This will confirm the thesis concerning the effect of temperature on the detonability of LNG and also test the importance and effect of composition.

As discussed in Section 4.0, the two cloud detonation transfer technique can be used to test the ability of unconfined chemical clouds to support detonation. By properly sizing both the driver and test cloud, the detonability of unconfined chemical clouds can be determined. This technique has advantages over the use of large quantities of high explosives to initiate the blast wave in the test cloud. We recommend that this technique be utilized to check or determine the detonation propagation of and effects on a variety of unconfined chemical clouds such as LNG and liquefied propane (LP).

6.0 References

1. A. L. Schneider, "Liquefied Natural Gas Safety Research Overview", US Coast Guard, Washington, DC; presented at the 1978 American Gas Association, Cryogenic Society of America LNG Terminal and Safety Symposium, San Diego, California; October 12-13, 1978.

2. D. C. Bull, J. E. Elsworth, G. Hooper, C. P. Quinn, J. Physics D, Volume 9, p. 1991, (1976).

3. A. A. Boni, C. W. Wilson, "A Study of Detonation in Methane/Air Clouds", presented at the Sixth International Colloquium on Gas Dynamics of Explosions and Reactive Systems". Stockholm, Sweden, August, 1977.

4. "Field Tests of Fuel/Air Explosives", Geo-Centers, Inc., Newton Upper Falls, MA 02164, Report No. GC-TR-78-1020, October, 1978. Submitted to Defense Advanced Research Projects Agency, Washington,DC.

5. J. Bowen, L. Cyrus, Naval Weapons Center, China Lake, California; (private communication).

6. C. W. Wilson, A. A. Boni, "Ambient Temperature Effects on Gas Phase Detonation Thresholds", Science Applications, Inc., La Jolla, California; preprint (private communication).

7. E. K. Dabora, AIAA J., Volume 10, p. 1384 (1972).

8. I. Zel'dovich, S. M. Kogarko, N. N. Semonov, Soviet Physics Tech. Phys., Volume 1, No. 8, p. 1689 (1956).

9. A. G. White, J. Chem. Soc., 121, 1688 (1922).

10. A. G. White, J. Chem. Soc., 127, 672 (1925).

11. H. Matsui, J. H. Lee, "On the Measure of the Relative Detonation Hazards of Gaseous Fuel-Oxygen and Air Mixtures, preprint from Dept. of Mechanical Engineering, McGill University, Montreal, Canada.

12. D. C. Bull, J. E. Elsworth, G. Hooper, Combustion and Flame, 34, 327 (1979).

Appendix A

Gas Chromatographic Analysis of LNG Samples

SUBJECT:	Analysis of LNG Samples
DATE OF ANALYSIS:	December 13, 1978
PROCEDURE:	Internal atmospheres of Sample Containers were analyzed via Gas Chromatography
RESULTS:	Given in Volume Percent

CH_4	99.75
O_2/Ar	trace
N_2	.02
C_2H_6	.18
C_3H_8	.03
C_4H_{10}	.01
C_4t	.01

SUBJECT:	Analysis of LNG Headspace Gas
DATE OF ANALYSIS:	December 18, 1978
PROCEDURE:	To more closely approximate actual composition, liquid in the LNG Dewar was allowed to vaporize directly through the sampling system; resulting in higher C_2-C_4 concentrations.
RESULTS:	Given in Volume Percent

CH_4	96.46
O_2/Ar	.02
N_2	.03
CO_2	.01
C_2H_6	2.83
C_3H_8	.48
C_4H_{10}	.09
C_4	.08

Appendix B

Temporal Dissemination Behavior of LNG

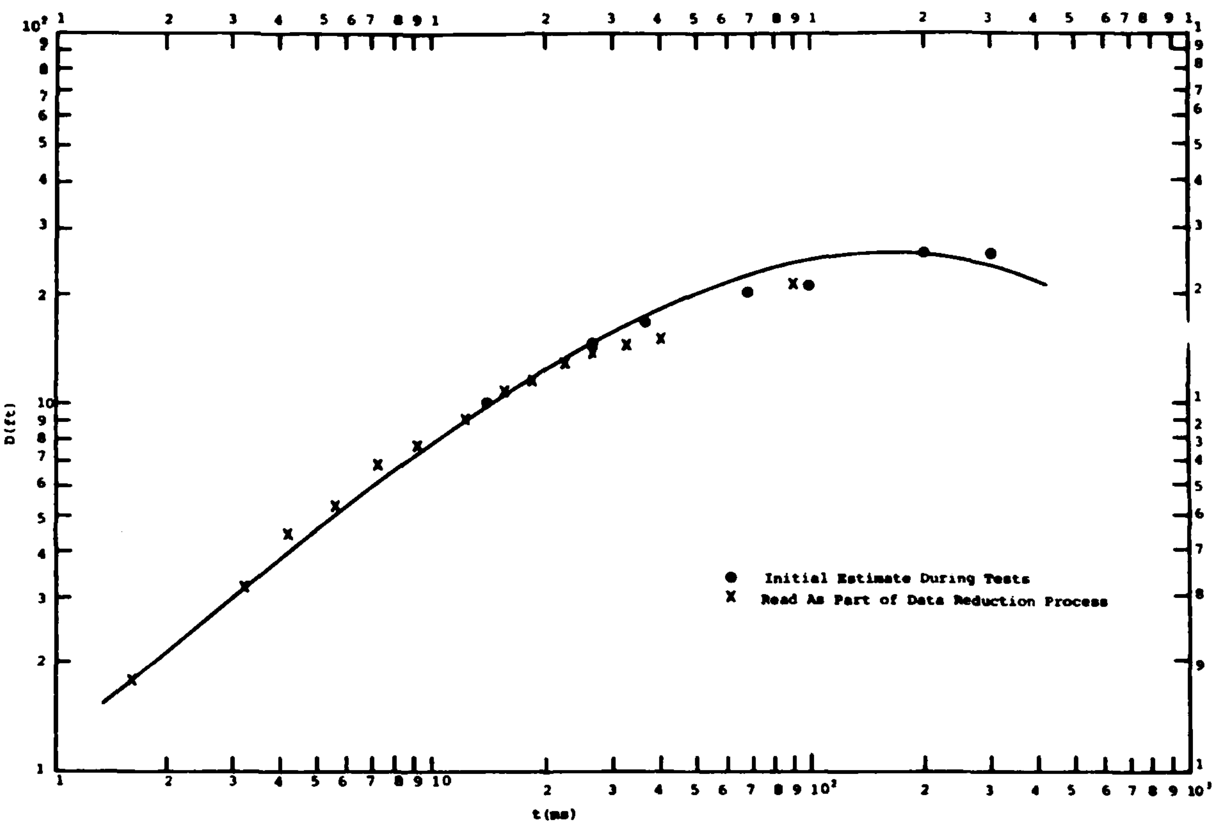


Figure B-1   LMG Dissemination, Test 1.

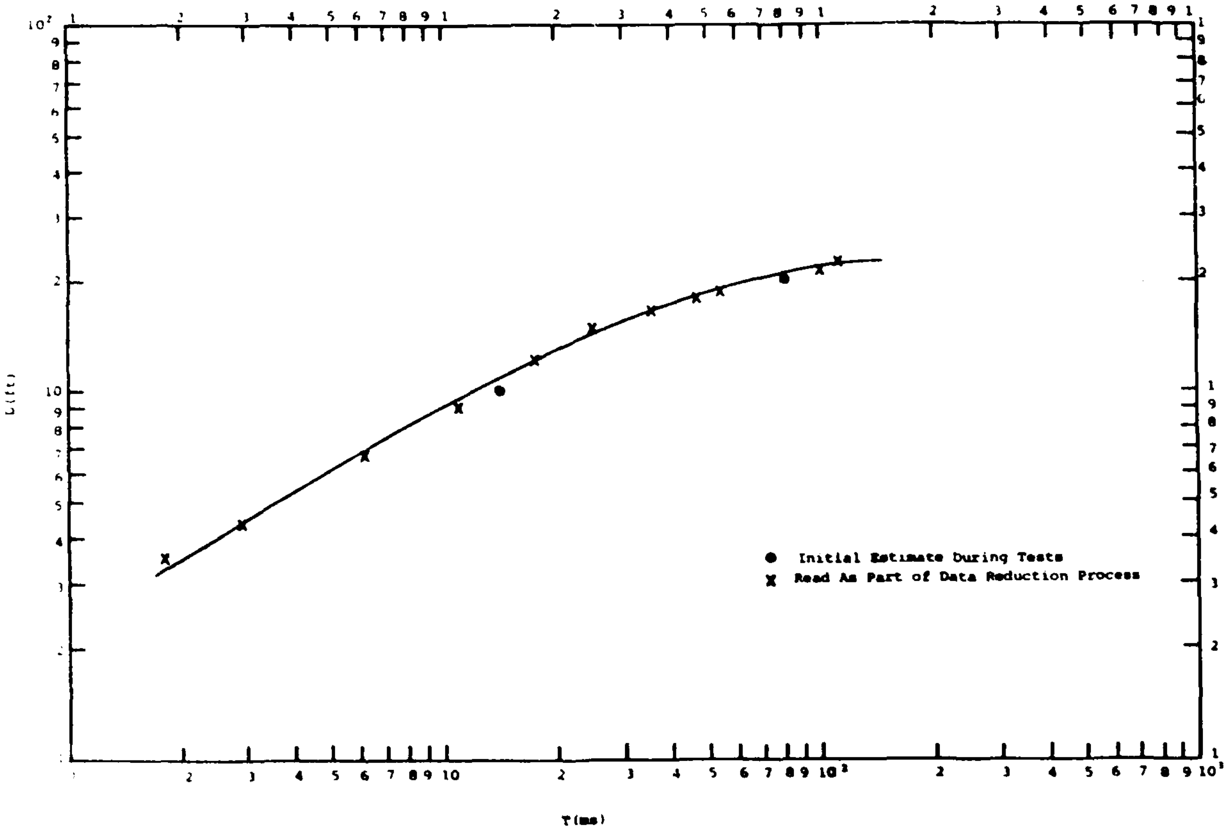
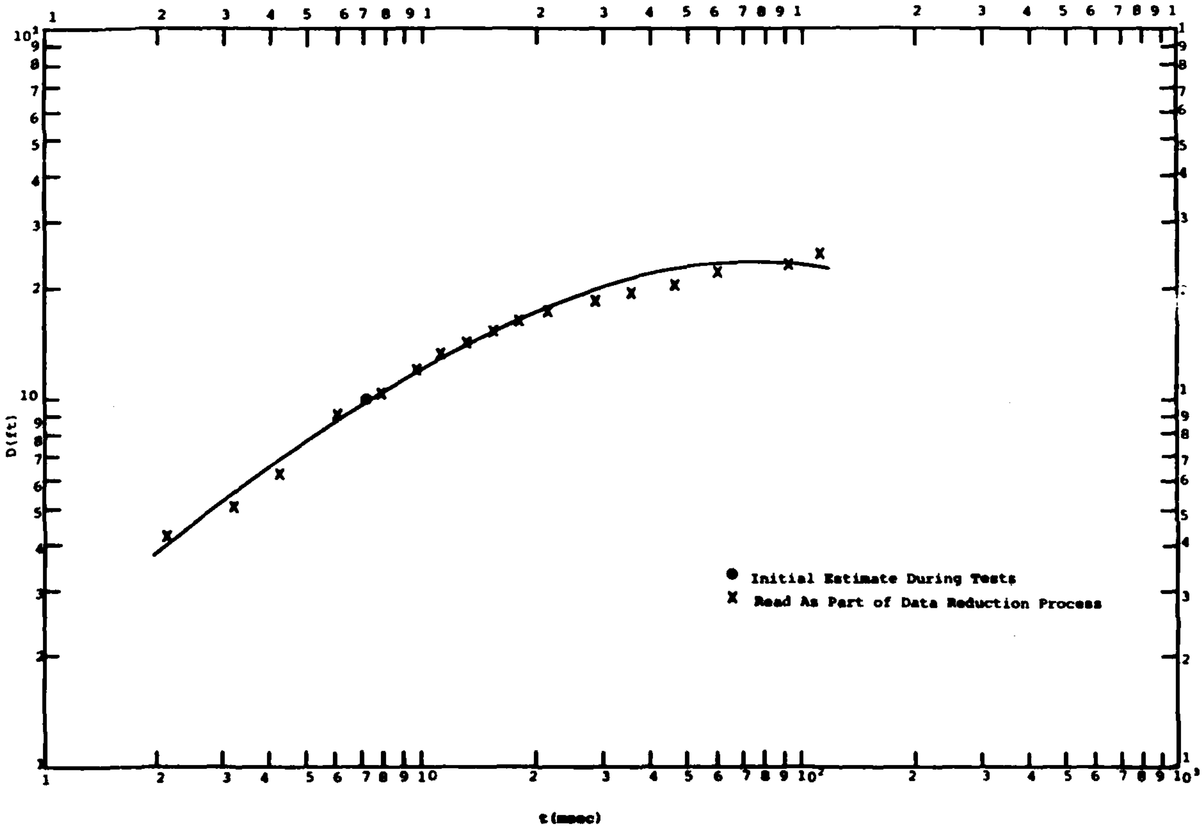


Figure B-2 LNG Dissemination, Test 2.



B-3 LNG Dissemination, Test 3

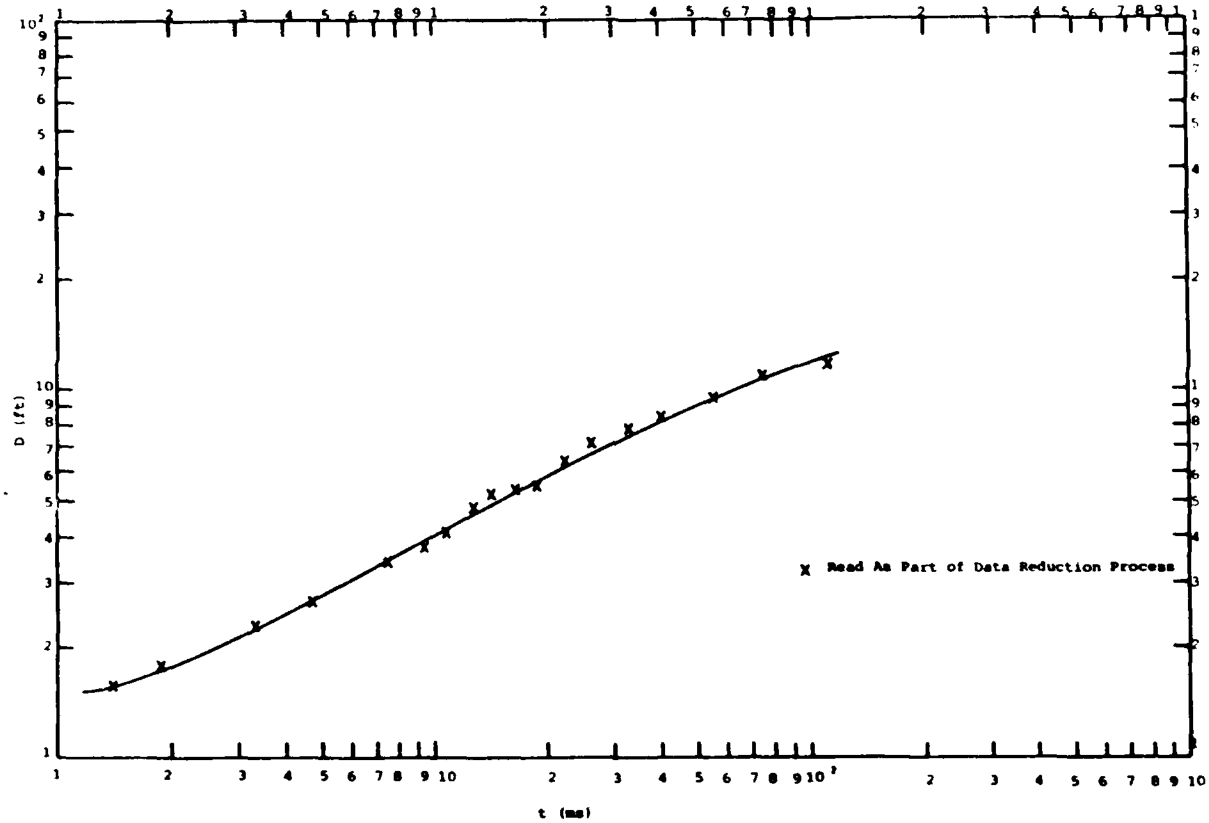
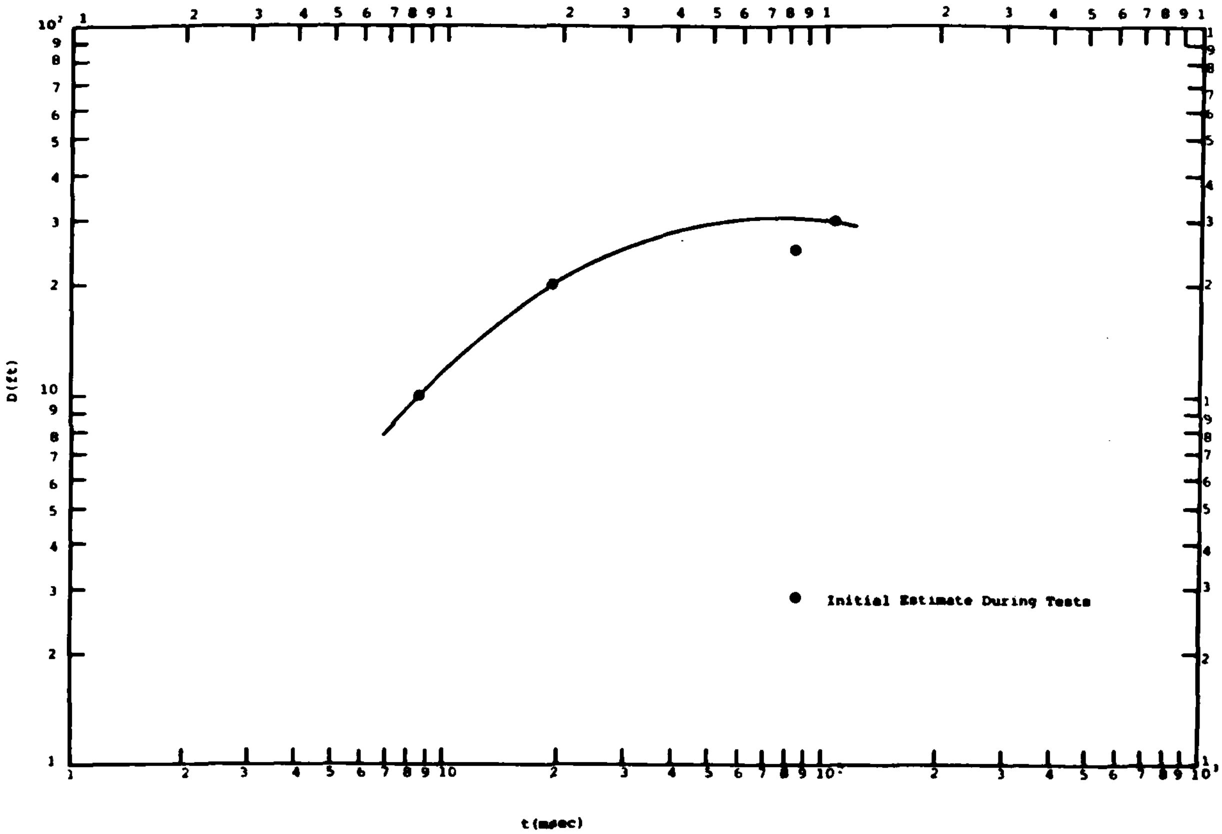


Figure B-4 LNG Dissemination, Test 4.



B-5 LNG Dissemination, Test 5

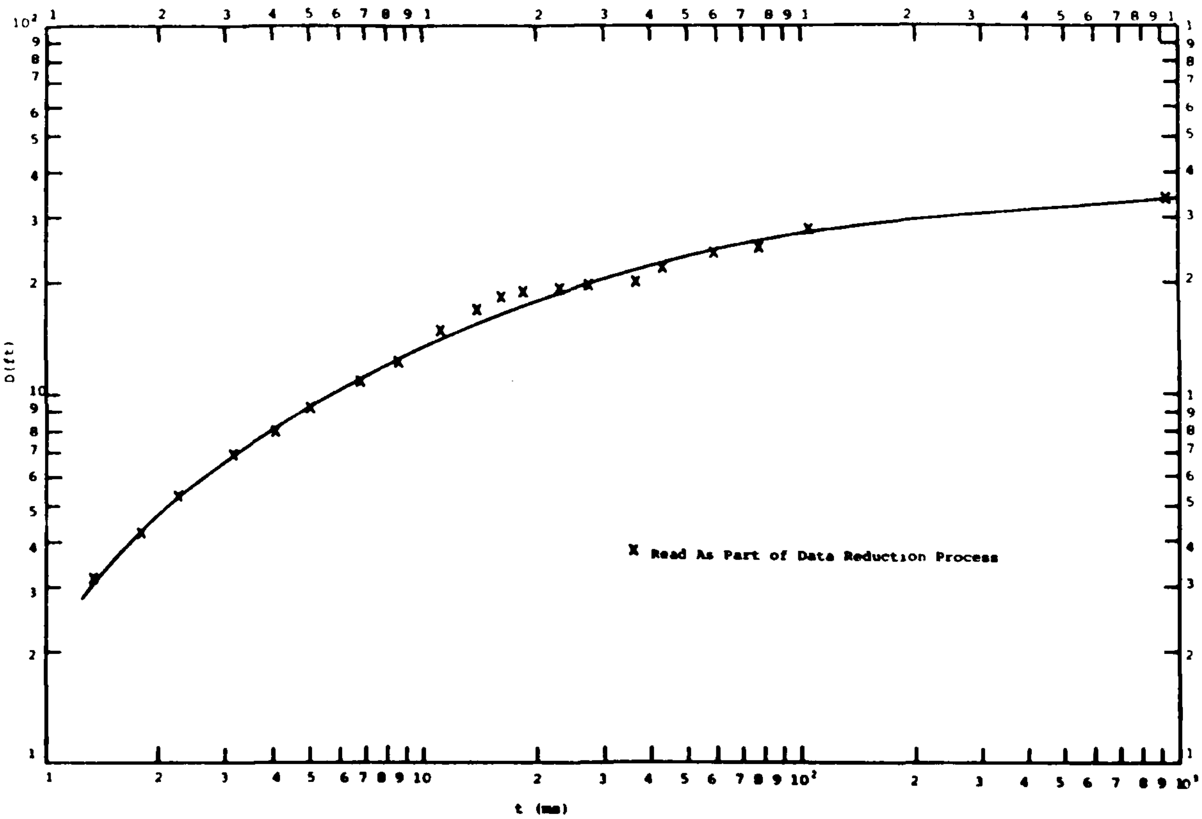


Figure B-6 LNG Dissemination, Test 6.

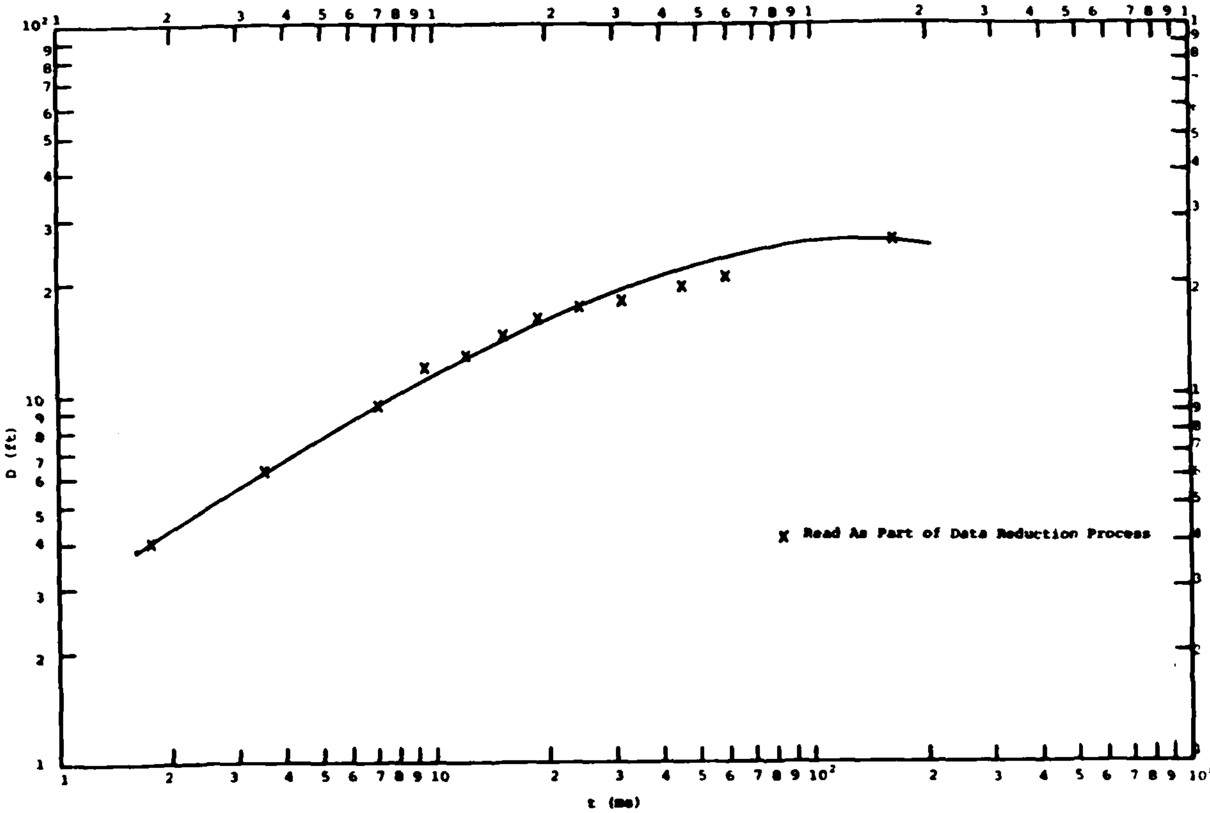


Figure B-7 LNG Dissemination, Test 7.